

EP



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

O 003 957

B1

⑬

EUROPEAN PATENT SPECIFICATION

⑭ Date of publication of patent specification: 29.09.82

⑮ Int. Cl.²: C 08 F 6/16, C 08 F 12/08,

⑯ Application number: 78300848.5

C 08 F 257/02, C 08 F 2/16

⑰ Date of filing: 18.12.78

⑲ Process for reducing the residual styrene level of a polystyrene latex.

⑳ Priority: 03.03.78 GB 854678

㉑ Proprietor: ISR HOLDING S.A.R.L.
15 Rue Notre Dame
L-Luxembourg (LU)

㉒ Date of publication of application:
19.09.79 Bulletin 79/19

㉓ Inventor: Moore, John David
9 Pear Tree Road Dibden Purlieu
Hythe Hampshire (GB)
Inventor: Feast, Alan Arthur John
3 Lakewood Road
Chandlers Ford Hampshire (GB)

㉔ Publication of the grant of the patent:
28.09.82 Bulletin 82/39

㉕ Designated Contracting States:
DE FR IT NL

㉖ Representative: Jones, Alan John et al.
CARPMAELS & RANSFORD 43 Bloomsbury
Square
London, WC1A 2RA (GB)

㉗ References cited:
DE - B - 1 292 848
FR - A - 377 425
FR - A - 2 005 711
US - A - 3 726 375
US - A - 4 011 283

EP 003 957

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 89(1) European patent convention).

Process for reducing the residual styrene level of a polystyrene latex

This invention relates to emulsion polymerisation processes which are carried out to a high conversion of styrene monomer to polymer.

In this specification the expression "emulsion polymerisation processes" includes both addition polymerisation processes and grafting processes which are carried out in emulsion.

Emulsion polymerisation processes have been employed for several decades in the preparation of polymers from vinyl and/or conjugated diene monomers. Initially such processes were used for the preparation of styrene-butadiene rubber (SBR). These processes were and still are generally carried out to a conversion of monomer to polymer of about 65% to maintain optimum properties in the rubber. More recently a wider range of emulsion polymerisation processes have been employed in the preparation of both solid polymers and polymer latices. In the preparation of many polymer latices it is possible to carry out the emulsion polymerisation process to high conversion levels, generally at least 90% without affecting adversely the properties of the latex. Polystyrene latices and carboxylated SBR latices are examples of such latices prepared by emulsion polymerisation. Acrylonitrile-butadiene-styrene (ABS) resins may be prepared by an emulsion grafting reaction likewise carried out to a high conversion.

No matter how high the conversion of monomer to polymer it is rarely possible or economic to achieve total conversion. There nearly always remains some residual monomer. This may be present in amounts of, for example, 0.5% to 5% or more. It is therefore usual to subject the latex to a stripping operation to remove the residual, unreacted monomer(s).

Even after such a stripping operation, residual monomer may remain in the latex, occluded in the polymer particles. Another disadvantage of the stripping stage is that capital investment for the equipment is required. Further, considerable amounts of energy are consumed in the operation since steam is normally employed. This is particularly the case where the monomer(s) to be stripped have a relatively high boiling point, for example, styrene (boiling point = 146°C), acrylonitrile (78°C) and methacrylic acid (163°C).

The present invention provides a process for reducing the residual styrene monomer level of a polymer latex prepared by a main emulsion polymerisation of styrene monomer or a monomeric mixture containing styrene monomer taken to a conversion of at least 90% characterised in that the polymer latex is exposed in a separate vessel from that in which the main polymerisation has been carried out to con-

ditions under which free radicals are produced by a secondary redox catalyst, said catalyst comprising an oil-soluble oxidising component and an activator component, at least one of which components is added to the latex subsequent to the main polymerisation.

By this process the residual monomer level may be reduced to very low levels, generally below 0.1%, without the need for a stripping stage. Of course, if desired, some stripping of the latex may be carried out, but this is not necessary to achieve very low residual monomer levels.

The process is particularly applicable to latices prepared by the emulsion polymerisation of styrene alone or of a monomer mixture containing styrene, for example, styrene/acrylonitrile and a mixture comprising butadiene, styrene and one or more unsaturated acids. Typical examples are carboxylated SBR latices and latices of ABS resins and polystyrene.

We believe that using an oil soluble oxidising component is advantageous since migration to the inside of the polymer particles containing the residual monomer occurs thus producing free radicals exactly where required. Further, redox catalysts having an oil soluble oxidising component give a more controlled generation of free radicals at the polymer particle/water interface than is obtained by thermal decomposition alone. Further, the decomposition may be obtained exactly when required simply by addition of the activator component whereas, with a thermally decomposable initiator, free radicals are generated as soon as the initiator is introduced into the latex. Therefore the use of a redox catalyst enables greater control to be exercised over the exposure of the latex to free radicals produced by the secondary catalyst.

Oil soluble oxidising components having a half life of longer than 4 hours at 100°C are employed in the redox system in combination with a water soluble activator, such as an amine, for example diethylene triamine (DET), triethylene tetramine (TET) or tetraethylene pentamine (TEP). Examples of such oxidising components are cumene hydroperoxide (CHP), tertiary-butyl hydroperoxide (TBHP), paramenthane hydroperoxides (PMHP) and diisopropyl benzene hydroperoxide (DIBHP). If ferrous iron has been used as part of the initiator of the main polymerisation, this will act as an activator to produce a secondary redox catalyst when the oxidising component is added. However, it is still preferable in such cases to employ an amine activator. Examples of amounts of oxidising component which may be used are up to about 0.50 parts per hundred parts by weight of polymer (0.5 php), typical amounts being 0.15 or 0.30 php. The activator

is preferably used in the weight ratio oxidising component to activator of, for example, 1:2 to 2:1.

The process is carried out in a separate vessel from that in which the main polymerisation has been carried out. This may be, for example, a storage vessel or unstirred tank. The main polymerisation may be a batch reaction or preferably a continuous reaction so that the vessel serves to receive the latex from the main polymerisation. The latex in the vessel is preferably at a temperature of 50°C or more, dependent upon the secondary catalyst employed, so that free radicals are produced without external heat being applied.

In the case of an activated cumene hydroperoxide as secondary catalyst a temperature of 70°C is very suitable. This enables a residual styrene content of 1.6% in a carboxylated latex to be reduced to about 0.02 to 0.05% or even less in about five hours. When treating a carboxylated latex (produced in acid medium) by the process of the invention it may be advantageous to increase the pH to, for example, about 9 by the addition of, for example, ammonia before adding the secondary catalyst, otherwise there is a risk of reaction between the solid latex and any alkaline component of the secondary catalyst, for example, diethylene triamine.

Although the latex is exposed to free radicals produced by the secondary catalyst in a separate vessel from that in which the main polymerisation has been carried out, it is not essential that the secondary catalyst is added to this separate vessel. Thus, provided that conditions under which free radicals are produced by the secondary catalyst are avoided in the main polymerisation, it is possible for one component of the secondary catalyst to be added with the monomers and other components of the main polymerisation. For example, a hydroperoxide with a long half life may be included with the reactor charge of the main polymerisation, the activator initiating the production of free radicals by the secondary catalyst being added to the latex after the latex has been removed from the vessel in which the main polymerisation has been carried out. In such cases the activator may be added to the separate vessel or to the pipe connecting the two vessels. The latter procedure may be advantageous since it enables a better dispersion of the activator into the latex to be obtained. However, if desired, the secondary catalyst or the components thereof may be added to the separate vessel directly. The addition of the secondary catalyst or one or both components thereof may be carried out continuously or incrementally as desired. Continuous addition is preferable when the main polymerisation is carried out continuously.

It will be understood that the latex can be withdrawn from the vessel in which the main polymerisation has been carried out at any

desired conversion. Thus it is not necessary to delay withdrawal until a conversion of 90% or more has been achieved. Thus the latex may be withdrawn at a conversion level of, for example, 80% and, when a conversion of at least 90% has been achieved, then treated by the process of the present invention in the separate vessel. It may well be that in most cases polymerisation would continue beyond 90% conversion in the separate vessel without the addition of a secondary catalyst. However, exposure of the latex to conditions under which free radicals are produced by a secondary catalyst formed in the latex in accordance with our invention enables the conversion of monomer to polymer to be carried out to a very high level, thus reducing the residual monomer level to a very low figure, generally not exceeding 0.1%. This is achieved both conveniently and economically. Very low residual monomer contents are increasingly required to meet present day health and safety standards.

The following Examples illustrate the invention.

(In these Examples references to parts are references to parts by weight per hundred parts dry weight of polymer — php).

Example 1

A carboxylated styrene butadiene copolymer latex containing 60% bound styrene was prepared at 70°C to 90°C using ammonium persulphate as the initiator. After polymerisation the residual styrene content was analysed at 1.06% (based on the latex volume).

(a) A portion of this latex was treated with ammonia to adjust the pH to 9.0 and was then treated with a secondary catalyst comprising cumene hydroperoxide 0.16 parts and diethylene triamine 0.12 parts. This treated latex was then heated for 5 hours at 70°C. It was found that the residual styrene content had been reduced to 0.02%.

(b) For comparison the procedure of Example 1(a) was repeated using a water soluble catalyst (ammonium persulphate 0.15 parts and 0.3 parts). It was found that the residual styrene content was reduced to 0.2% in each case.

Example 2

A carboxylated styrene butadiene copolymer latex containing 50% bound styrene was prepared as in Example 1. After polymerisation the residual styrene content was analysed at 0.6% (based on latex volume).

(a) A portion of this latex was treated with ammonia to increase the pH to 9.5 and then treated with a secondary catalyst comprising cumene hydroperoxide 0.16 parts and diethylene triamine 0.08 parts. The treated latex was heated for 15 hours at 70°C to 90°C. It was found that the residual styrene content had been reduced to 0.01%.

(b) For comparison the procedure of Example 2(a) was repeated using ammonium per-

sulphate 0.15 parts and 0.3 parts, it was found that the residual styrene content was reduced to 0.2% in each case.

Example 3

A polystyrene latex was prepared using ammonium persulphate as initiator. After polymerisation the residual styrene content was analysed at 1.2 to 3.0% (based on the latex volume).

(a) A portion of this latex was treated with a secondary catalyst comprising cumene hydroperoxide 0.16 parts and diethylene triamine 0.12 parts. This was added to a separate vessel from that in which the main polymerisation had been carried out, the polymerisation still continuing in the separate vessel. After heating for 4 hours at 93°C it was found that the residual monomer level was 0.1%.

(b) For comparison the procedure of Example 3(a) was repeated using ammonium per-

sulphate 0.2 parts. The residual styrene content was reduced to 0.3%.

Example 4

5 Samples of an acrylonitrile-butadiene-styrene latex were prepared by grafting styrene and acrylonitrile on to polybutadiene latex in a continuous emulsion polymerisation at 85°C to 100°C using an initiator of cumene hydroperoxide and ferrous iron/glucose activator. After polymerisation the latex samples were analysed for styrene and acrylonitrile, the levels of each being indicated in the table, (per cent based on latex volume).

10 A secondary catalyst of cumene hydroperoxide (0.16 phr) and diethylene triamine (0.08 phr) was added to each and the latex samples heated for 4 hours at 85°C. This treatment gave a marked reduction both in residual styrene and acrylonitrile levels as shown in the table.

TABLE

ABS Samples	Residual monomer			
	After main polymerisation		Secondary catalysis using CHP/DET 4 hrs., 85°C	
	% Styrene	% ACN	% Styrene	% ACN
1	0.8	0.74	0.09	0.13
2	0.52	0.55	0.08	0.14

Claims

1. A process for reducing the residual styrene monomer level of a polymer latex prepared by a main emulsion polymerisation of styrene monomer or a monomeric mixture containing styrene monomer taken to a conversion of at least 90% characterised in that the polymer latex is exposed in a separate vessel from that in which the main polymerisation has been carried out to conditions under which free radicals are produced by a secondary redox catalyst, said catalyst comprising an oil-soluble oxidising component and an activator component, at least one of which components is added to the latex subsequent to the main polymerisation.

2. A process according to Claim 1 characterised in that the oil-soluble oxidising component is cumene hydroperoxide, tertiary-butyl hydroperoxide, paramenthane hydroperoxide or diisopropylbenzene hydroperoxide.

3. A process according to Claim 1 or Claim 2 characterised in that the activator component is

diethylene triamine, triethylene tetramine or tetraethylene pentamine.

4. A process according to any one of Claims 1 to 3 characterised in that the oil-soluble oxidising component of the redox catalyst is included with the reactor charge of the main polymerisation and the activator component which initiates the production of free radicals by the secondary redox catalyst is added to the latex after the latex has been removed from the vessel in which the main polymerisation has been carried out.

5. A process according to any one of Claims 1 to 4 wherein the latex is a carboxylated SBR latex, an ABS resin latex or a polystyrene latex.

6. A process according to any one of Claims 1 to 5 characterised in that the residual styrene monomer is reduced to a level not exceeding 0.1% based on latex volume.

Revendications

65 1. Propédé pour abaisser le taux de mono-

mère de styrène résiduel d'un latex de polymère préparé par une polymérisation principale en émulsion de monomère de styrène ou d'un mélange monomère contenant du monomère de styrène porté jusqu'à une conversion d'au moins 90%, caractérisé en ce que le latex de polymère est exposé, dans une cuve séparée de celle dans laquelle a eu lieu la polymérisation principale, à des conditions dans lesquelles des radicaux libres sont produits par un catalyseur redox secondaire, ledit catalyseur comprenant un constituant oxydant soluble dans l'huile et un constituant d'activation, au moins un des constituants étant ajouté au latex, après la polymérisation principale.

2. Procédé selon la revendication 1, caractérisé en ce que le constituant oxydant soluble dans l'huile est l'hydroperoxyde de cumène, l'hydroperoxyde de butyle tertiaire, l'hydroperoxyde de paramenthane ou l'hydroperoxyde de diisopropylbenzéne.

3. Procédé selon l'une des revendications 1 ou 2, caractérisé en ce que le constituant d'activation est la diéthylène triamine, la triéthylène tétramine ou la tétréthylène pentamine.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que le constituant oxydant soluble dans l'huile du catalyseur redox est incorporé avec la charge du réacteur de la polymérisation principale et le constituant d'activation qui initie la production de radicaux libres par le catalyseur redox secondaire est ajouté au latex après qu'il a été sorti de la cuve dans laquelle a eu lieu la polymérisation principale.

5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le latex est un latex de SBR carboxylié, un latex de résine d'ABS ou un latex de polystyrène.

6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que le monomère de styrène résiduel est abaissé à un taux ne dépassant pas 0,1% par rapport au volume de latex.

Patentansprüche

1. Verfahren zur Herabsetzung des Reststyrolmonomergehaltes eines Polymerlatex, der durch eine Hauptemulsionspolymerisation von Styrolmonomerem oder einer Monomerenmischung, die Styrolmonomerem enthält und auf einen Umsatz von wenigstens 90% ausgelegt ist, hergestellt worden ist, dadurch gekennzeichnet, daß der Polymerlatex in einem anderen Gefäß als das Gefäß, in dem die Hauptpolymerisation durchgeführt worden ist, Bedingungen ausgesetzt wird, unter denen freie Radikale durch einen sekundären Redox-Katalysator erzeugt werden, wobei der Katalysator eine ölföllösliche oxidierende Komponente und einen Aktivatorkomponenten aufweist, wobei wenigstens eine dieser Komponenten dem Latex anschließend an die Hauptpolymerisation zugesetzt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die ölföllösliche oxidierende Komponente aus Cumolhydroperoxid, tert-Butylhydroperoxid, p-Menthanylhydroperoxid oder Diisopropylbenzolhydroperoxid besteht.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Aktivatorkomponente aus Diäthylentriamin, Triethylentetramin oder Tetraäthylpentamin besteht.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die ölföllösliche oxidierende Komponente des Redox-Katalysators der Reaktorcharge der Hauptpolymerisation und die Aktivatorkomponente, welche die Erzeugung von freien Radikalen durch den sekundären Redox-Katalysator injiziert, dem Latex zugesetzt wird, nachdem der Latex aus dem Gefäß entfernt worden ist, in welchem die Hauptpolymerisation durchgeführt worden ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß der Latex ein carboxylierter SBR-Latex, ein ABS-Harzlatex oder Polystyrollatex ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß der Rest Styrolmonomergehalt auf einen Wert herabgesetzt wird, der 0,1% bezogen auf das Latexvolumen, nicht übersteigt.

50

55

60

65

5